

ULTRAVIOLET-CURED COATINGS WITHOUT USE OF ACRYLATES

5700

Abstract

Although leather coatings have been prepared by ultraviolet (UV) irradiation of solvent free, 100% reactive acrylate systems, a process which eliminates air pollution and conserves energy, their industrial adoption has been impeded because of possible toxicity of acrylate chemicals. The coatings described here were prepared from non-acrylic oligomers containing maleate and vinyl functionality, which cure rapidly after exposure to UV light. Odorless coatings were formed with good abrasion resistance. Their flexibility was improved by adjustment of formulation. Other physical properties of these coatings including tensile strength and percent elongation are compared with those obtained from acrylate formulations used as reference.

Introduction

The use of ultraviolet light to cure solvent-free leather finishes has among its advantages: reduction of air pollution, lower energy costs and good physical properties of the final product. However, among the disadvantages of this process is that a principal part of radiation curable formulations are acrylate compounds. These have been cited as potential health hazards⁽¹⁾. Although acrylates continue to be the most important component of 100% solids systems because of their fast cure by UV or electron-beam irradiation, efforts have been made to develop alternatives or substitutes. This had led to preparation and manufacture of prepolymers and oligomers end-capped with maleate groups⁽²⁾ and to urethane oligomers functionalized with vinyl ether groups^(3,4). Preliminary testing has indicated that maleate oligomers and vinyl ethers cause minimal eye and skin irritation and are non-mutagenic^(2,3). Although these new materials have been developed for preparation of non-acrylate polymers, their application as potential coatings for leather has not been studied.

Experimental

MATERIALS AND METHODS

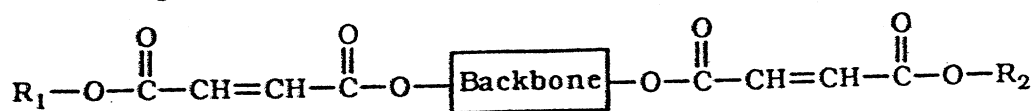
All chemicals were obtained from commercial sources and were used as received. Non-acrylate oligomers including Desolite 1100, 1110, 1115, 1200 and 1300 were obtained from DSM Desotech, Inc., Des Plaines, IL. Vinyl ether oligomer (Vectomer 2020) and reactive diluents (Vectomer 4010 and 4020) were from Allied-Signal Corp., Morristown, NJ. The reactive diluent triethylene glycol divinyl ether (DVE-3) was obtained from GAF Chemicals Corp., Wayne, NJ. Darocur photoinitiator was purchased from EM Industries, Inc., Hawthorne, NY, sulfonium initiator UVI-6974 from Union Carbide Corp., Danbury, CT, and phenothiazine inhibitor from Aldrich Chemical Co., Milwaukee, WI. Ebecryl 6700, an acrylated urethane oligomer, was furnished by Radcure Specialties, Louisville, KY, and isodecyl acrylate by Sartomer, Exton, PA.

Formulations were applied with wire wound, stainless steel rods (R.D. Specialties, Webster, NY) that delivered metered (0.54 mil) thicknesses of coatings to black side leather which lacked topcoats and 6.75 mil coatings to glass plates. Ultraviolet radiation was carried out with a conveyORIZED system, Model F440, from Fusion Systems Corporation, Rockville, MD. It included two electrodeless, microwave activated, 300 watts/inch "D" lamps with principal radiation at 350-400 nm, 10 in. in length, operated in series at a belt speed of 30 ft/min. In every case, two passes under the lights were carried out to ensure complete cure.

The finished coatings were conditioned for 24-48 hr at 70°F and 50% relative humidity and evaluated. Flexibility of the leather was determined with a Bally Flexometer, Model STM 407. Dry test pieces, 7.0 x 4.5 cm were used. The principal damage observed was cracking of the finish, which was recorded with the corresponding number of cycles. Resistance to abrasion was measured using a Taber Abraser, Model 503, with CS-10 wheels and a 500 g load. Cast films (6.75 mil thick) were tested for tensile strength and percent elongation with an Instron Universal Tester, Model 1122 and a Keithley PC interface. Data obtained were analyzed using a sequence of BASIC and Lotus 1-2-3 programs.

Discussion

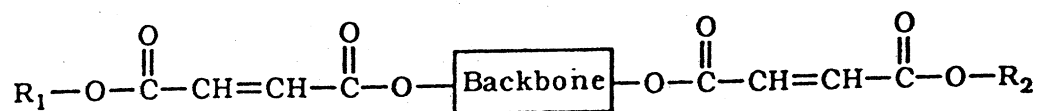
In initial experiments, non-acrylate oligomers containing maleate groups as reactive sites were used. A series of these oligomers is available commercially from DSM Desotech, Inc. and has the generalized structure shown below:



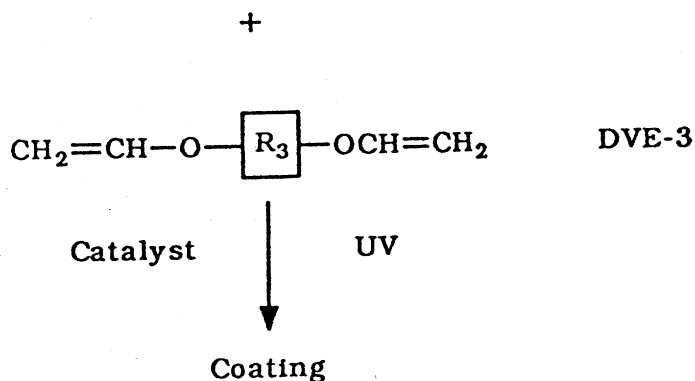
The backbone may have different structures including saturated polyesters, urethanes or epoxides. Each of these types was used in our investigation. The maleate oligomers were crosslinked by free-radical reaction with triethylene glycol divinyl ether, DVE-3, catalyzed by UV light with 3% Darocur 1173 as initiator. A generalized equation is given in Figure 1. The formulations tested (Table I) used equivalent amounts of the maleate ethers and DVE-3 with 3% (wt) photoinitiator. It was advantageous to add a small amount of antioxidant such as hydroquinone or phenothiazine to increase the stability of the mixture.

In every case the solution could be readily applied to leather or to glass plates with the

FIG. 1. — General equation for use of maleate oligomer.



Typical Maleate End-Capped Oligomer



drawdown rods previously mentioned. Cure with UV light was instantaneous and led to tack-free, odorless coatings with a bright, glossy appearance. Although each of the leather samples showed good resistance to Taber abrasion, it was obvious that the coatings were quite brittle and cracked easily with mild flexing. A summary of the physical properties of the leather finished with maleate coatings from reaction of 1 equivalent of maleate and 1 equivalent DVE-3 is given in Table II.

Because of the apparent superiority with respect to appearance and abrasion resistance of coatings prepared from urethanes end-capped with maleate groups, an additional series of coatings was prepared using Urethane 1200 as the oligomer in each formulation. In order to increase the flexibility of the final coating or film, the ratio of oligomer: DVE-3 was changed from 1:1 as shown in Table I to 1:2, 1:3, 1:4 and 1:5. In each case 3% Darocur 1173 photoinitiator was added. These formulations are summarized in Table III.

TABLE I

Formulations with Maleate Oligomers

Oligomer	Ester 1100	Ester 1110	Ester 1115	Urethane 1200	Epoxy 1300
Functionality	4	2	2	2	2
Equivalents	1	1	1	1	1
Oligomer					
Equivalents DVE-3	1	1	1	1	1
Catalyst (%)	3	3	3	3	3

TABLE II

Physical Properties of Maleate Coatings
(1 equivalent maleate: 1 equivalent DVE-3)

Oligomer	Ester 1100	Ester 1110	Ester 1115	Urethane 1200	Epoxy 1300
Appearance	Good	Good	Good	Excellent	Excellent
Flexibility	Poor	Poor	Poor	Poor	Poor
Abrasion Resistance	Good	Good	Good	Excellent	Good

TABLE III

Urethane Coatings with Varying Quantities of DVE-3*

Formulation	A	B	C	D	E
Equivalents Urethane 1200	1	1	1	1	1
Equivalents DVE-3	1	2	3	4	5

*3% Darocur 1173 catalyst.

TABLE IV

Comparative Properties of Non-Acrylate Films

Sample Formulation	Maximum Stiffness (N/nm)	Peak Stress (MPa)	Strain @ Peak Stress (%)	Work To Break (MPa-%)
Maleates				
Reference Film ^a	4.31 ± 0.62	169.09 ± 10.63	134.05 ± 7.69	15826.00 ± 1396.69
"B" Film ^b	18.24 ± 4.47	127.34 ± 51.71	4.25 ± 1.45	298.68 ± 184.81
"C" Film ^c	6.77 ± 0.81	81.66 ± 19.03	9.02 ± 2.58	472.45 ± 225.73
"D" Film ^d	1.60 ± 0.63	9.88 ± 2.08	2.44 ± 1.08	14.96 ± 7.79
"E" Film ^e	1.29 ± 0.13	6.95 ± 1.57	2.78 ± 0.96	10.59 ± 4.24
Ester 1100	13.61 ± 1.56	119.70 ± 34.78	4.68 ± 1.89	388.81 ± 262.35
Epoxy 1300	26.78 ± 3.45	185.83 ± 41.64	3.85 ± 0.75	382.35 ± 120.08
Cationics				
Aliphatic	0.54 ± 0.07	55.88 ± 4.54	35.19 ± 9.80	1650.32 ± 540.05
Aromatic	0.39 ± 0.09	53.06 ± 4.02	39.88 ± 5.62	1778.82 ± 332.47

^a 1:1:1 acrylated urethane : n-vinyl pyrrolidone : isodecyl acrylate + 3% Darocur

^b 1:2 urethane : divinyl ether + 3% Darocur

^c 1:3 urethane : divinyl ether + 3% Darocur

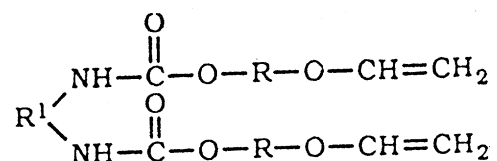
^d 1:4 urethane : divinyl ether + 3% Darocur

^e 1:5 urethane : divinyl ether + 3% Darocur

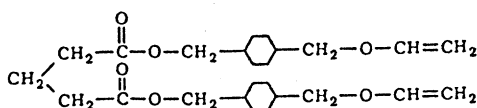
The effect of addition of excess DVE-3 was dramatic. The flexibility of the finished leathers was markedly improved. However, examination of stress-strain data obtained by Instron testing of the films (see Table IV) showed a considerable loss in strength as the proportion of DVE-3 was increased. For comparison, the same properties were determined on a 6.75 mil film cast from a mixture containing equal weights of an acrylated urethane

oligomer (Ebecryl-6700), N-vinyl pyrrolidone and isodecyl acrylate plus 3% Darocur 1173 initiator and cured as above. The acrylate-based films were markedly stronger.

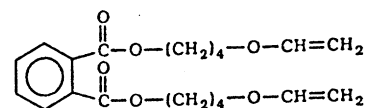
In a different approach to the preparation of non-acrylate UV-cured leather coatings, we have used a urethane oligomer functionalized with vinyl ether groups and cationically polymerized. In contrast to free-radically catalyzed systems, cationic systems require the presence of onium salt catalysts, which liberate strong acids (HX) when irradiated with UV light. The method has been used extensively to polymerize vinyl ether monomers⁽⁵⁾. Lapin and coworkers have described the preparation of vinyl ether urethane oligomers⁽³⁾ and their cationic cure with vinyl ether terminated ester monomers⁽⁴⁾. The latter monomers were used as reactive diluents along with DVE-3 and other vinyl ethers. For our purposes we tested one oligomer, Vectomer 2020, a difunctional aliphatic urethane oligomer terminated with vinyl groups:



and two reactive diluents, 4020 (a vinyl ether of an aliphatic ester) and 4010 (a vinyl ether of an aromatic ester). Both structures are given below:



4020



4010

The formulation with each reactive diluent is given below:

System A		System B	
Urethane oligomer	50% (wt)	Urethane oligomer	50% (wt)
Aliphatic diluent 4020	30%	Aromatic diluent 4010	30%
DVE-3 diluent	19%	DVE-3 diluent	19%
Cationic initiator	1%	Cationic initiator	1%

Once again the mixtures were applied at thicknesses of 0.54 mil as final coats for leather and at thicknesses of 6.75 mil on plate glass and cured by UV light (2 passes) at a belt speed of 30 ft/min. The finished leather has good abrasion resistance and flexibility. Both formulations cured rapidly and produced odorless, tack-free films on glass with a distinct tan coloration. Their stress-strain properties (Table IV) were inferior to those of the acrylate-based film used as a reference.

Conclusions

Coatings for leather can be prepared by ultraviolet radiation of 100% solids systems without the use of acrylates. Cure is instantaneous with free radical or cationic initiation. Odorless, tack-free products are obtained. However, film properties of the initial systems studied appear to be inferior to those from acrylates. Further research is needed to study factors such as application techniques, pigmentation, and improvement of physical performance of acrylate-free coatings.

References

1. Tu, R.S., "UV Curing: Science and Technology", S.P. Pappas (ed.), Technology Marketing Corp., Norwalk, Connecticut, 147 (1985).
2. Noren, G.K., Tortorello, A.J. and Vandeberg, J.T., Proceedings of RadTech '90, Volume 2, 201 (1990).
3. Lapin, S.C., Proceedings of RadTech '88, 395 (1988).
4. Brautigan, R.J., Lapin, S.C. and Synder, J.R., Proceedings of RadTech '90, Volume 1, 99 (1990).
5. Crivello, J.V., Lee, J.L. and Conlon, D.A., Proceedings of Radiation Curing VI, Association of Finishing Processes, Chicago, 4-28 (1982).

Discussion

DR. JERRY LEVY, Stahl Finish, USA: Would you know if the maleates and the vinyl ethers are Ames negative — have they been tested for mutagenicity in the Ames test?

DR. SCHOLNICK: No. As far as I know they have not yet been tested and this is what I alluded to in the beginning. Right now they're advertised as being safe and nontoxic, but I have no information that the Ames test has been run.

DR. LEVY: There's a long history of using maleates in the UV cure polyester field. I don't know what the testing results are on those, and there's also an equally long history, perhaps even longer, of using cinnamates in coatings for manufacture of printed circuit boards. And, I believe there should be some information on those kinds of materials concerning their toxicity in tests such as the Ames test.

DR. SCHOLNICK: I agree and I think it's something that will have to be investigated or divulged.

DR. WOLFGANG WENZEL, Bayer AG: Did you ever look at the color coats or just clear coats?

DR. SCHOLNICK: In the past, we have done some work with color coats. They cure well provided we used organic dyes. It doesn't work too well with pigments. The dyes cure very very nicely and instantaneously. We've reported on these in the past.

MR. TERRENCE WELCH, Prime Leather Finishes: Did you ever try recoating any of the pieces that you've finished?

DR. SCHOLNICK: No, I did not. Why?

MR. WELCH: Do you think you'd be able to get an innercoat adhesion between the two coats?

DR. SCHOLNICK: Oh, I see what you mean.

MR. WELCH: Because of the fact that UV ties up so tight.

DR. SCHOLNICK: Well, I don't know what's going to happen. In the past, with our previous formulations we've put on additional coats and they adhere very well. With these maleates or the cationic materials, I don't know. I really can't answer your question.